



TITLE:

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CITATION:

Yamamoto, M ...[et al]. Ag K- and L3-edge XAFS study on Ag species in Ag/Ga₂O₃ photocatalysts. Journal of Physics: Conference Series 2016, 712: 012074.

ISSUE DATE:

2016-05

URL:

<http://hdl.handle.net/2433/225083>

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2016 J. Phys.: Conf. Ser. 712 012074

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Ag K- and L₃-edge XAFS study on Ag species in Ag/Ga₂O₃ photocatalysts

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Abstract. Ag loaded Ga₂O₃ (Ag/Ga₂O₃) shows photocatalytic activity for reduction of CO₂ with water. Ag L₃-edge XANES and K-edge EXAFS spectra were measured for various Ag/Ga₂O₃ samples, which suggested that structural and chemical states of Ag species varied with the loading amount of Ag and the preparation method. The Ag species were metallic Ag particles with an AgGaO₂-like interface structure in the sample with high loading amount of Ag while predominantly Ag metal clusters in the sample with low loading amount of Ag. The XANES feature just above the edge represented the interaction between the Ag species and the Ga₂O₃ surface, showing that the Ag metal clusters had more electrons in the *d*-orbitals by interacting with the Ga₂O₃ surface, which would contribute the high photocatalytic activity.

1. Introduction

An increasing concentration of atmospheric CO₂ has become a concern for our planet. One of the solutions for this problem, photocatalytic reduction of CO₂ to other useful chemicals has attracted much attention [1–4]. For the CO₂ reduction, an external energy and an appropriate catalyst are required, since CO₂ is one of the most stable molecules. Recently, it has been reported that Ag loaded Ga₂O₃ (Ag/Ga₂O₃) shows the photocatalytic activity for reduction of CO₂ with water to produce CO [5–7]. In our previous study [8], we found that the chemical state of Ag species in as-prepared Ag/Ga₂O₃ samples affected the formation process of the reaction intermediate, which were closely related to the CO production efficiency. However, it is still unclear how the structural and chemical states of the Ag species as well as Ag–Ga₂O₃ interaction change with the loading amount of Ag. In the present study, Ag L₃-edge and K-edge XAFS analysis was applied to investigate the structural and chemical states of the Ag species, which provided us meaningful information for understanding the photocatalysis of Ag/Ga₂O₃ samples.



2. Experimental

Ag/Ga₂O₃ samples were prepared by an impregnation (IMP) method and a photodeposition (PD) method. Generally, it is expected that IMP method provides Ag ions well interacting with the Ga₂O₃ support while PD method is suited to the formation of metallic Ag species. For IMP method, a mixture of Ga₂O₃ powders and an aqueous solution of AgNO₃ was magnetically stirred and dried, followed by calcination at 673 K for 2 h. The loading amounts of Ag were 0.1, 0.2, 0.5, 1.0 and 5.0 wt%. For PD method, a mixture of a Ga₂O₃ powder and an aqueous solution of AgNO₃ with ethanol was magnetically stirred and photoirradiated for 3 h, followed by filtration. The loading amounts of Ag were 0.1 and 1.0 wt%. Ag L₃-edge XAFS measurements were carried out in a fluorescent X-ray yield mode and in a total electron yield mode at the beam line 6N1 at the Aichi Synchrotron Radiation Center (Proposal No. 2503042). Ag K-edge XAFS spectra were measured at the NW10A station at the Photon Factory in the High Energy Accelerator Research Organization in the fluorescence mode with a 19 element solid state Ge detector and in a transmission mode (Proposal No. 2014G547).

3. Results and discussion

In our previous study [8], TEM and HAADF-STEM measurements revealed that around 1 nm sized Ag clusters were formed predominantly in a 0.1 wt% Ag/Ga₂O₃ (IMP) photocatalytic active sample while Ag particles with the size of several–several tens nm in a 1.0 wt% Ag/Ga₂O₃ (IMP) sample. In a 5.0 wt% Ag/Ga₂O₃ (IMP) sample and a 1.0 wt% Ag/Ga₂O₃ (PD) sample, large Ag particles with the size of over 30 nm were observed. After heating the 1.0 wt% Ag/Ga₂O₃ (PD) sample at 673 K for 2 h, the average Ag particle size became smaller as 1–2 nm and they were highly dispersed on the Ga₂O₃ surface.

In the present study, the Ag species in the Ag/Ga₂O₃ samples were investigated in detail by Ag L₃- and K-edge XAFS spectroscopy. Figure 1 shows the spectra of the Ag/Ga₂O₃ samples together with Ag foil and Ag₂O as references. We tried to simulate the XANES spectra of the Ag/Ga₂O₃ samples by using the reference spectra, but the fitting was not sufficient, indicating that the Ag species in the Ag/Ga₂O₃ samples were not a simple mixture of metal and oxides. As is evident from figure 1, the XANES spectrum of the 0.1 wt% Ag/Ga₂O₃ (IMP) sample has no distinct peaks, which originates from highly dispersed Ag species such as 1 nm sized Ag clusters [8]. With increasing the loading amount of Ag, the feature of XANES changed gradually to the characteristic one of an Ag bulk.

Note that the peak at 3353 eV grew with the loading amount of Ag up to 1.0 wt%, and then decreased with 5.0 wt% loading. This peak has been assigned to the transition from 2p to unoccupied 4d states [9]. The peak was clearly shown in the spectrum of Ag₂O. Therefore, in the Ag/Ga₂O₃ samples with higher loading amount of Ag up to 1.0 wt%, most of Ag species would be partially oxidized. As for the 5.0 wt% Ag/Ga₂O₃, XANES spectra could be measured both in a fluorescent X-ray yield mode (FY) and a surface sensitive total electron yield mode (TEY) as shown in figures 1e and 1f. The former spectrum (FY) was similar to that of an Ag bulk, suggesting that Ag species was metallic. Nevertheless, a small peak at 3353 eV evidenced the existence of oxides. In the latter spectrum (TEY), this peak was clearly seen and more thorough observation suggested that double peaks at 3364 and 3380 eV became intense, which were similar to the characteristic feature of 1.0 wt% Ag/Ga₂O₃. This result indicates that the Ag species in the 5.0 wt% Ag/Ga₂O₃ sample is almost metallic Ag like an Ag bulk, but the surface is slightly oxidized. In addition, it is also suggested that the Ag species in 1.0 wt% Ag/Ga₂O₃ would be partially oxidized Ag particles or a mixture of the metallic and oxidized species, which will be discussed below.

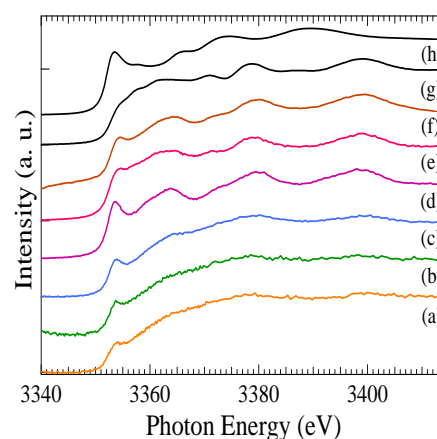


Figure 1. Ag L₃-edge XANES spectra of the Ag/Ga₂O₃ (IMP) samples (a–f), Ag foil (g) and Ag₂O (h). Ag loading (wt%): 0.1 (a), 0.2 (b), 0.5 (c), 1.0 (d), 5.0 (FY) (e) and 5.0 (TEY) (f).

Figure S1 in the supporting information shows the Ag L_3 -edge XANES spectra of the 0.1 and 1.0 wt% Ag/Ga₂O₃ (PD) samples. Since both the spectra were very similar to that of an Ag bulk, the Ag species in the 0.1 and 1.0 wt% Ag/Ga₂O₃ (PD) samples were metallic Ag. It was also confirmed that the broad feature shown in the XANES of the 0.1 wt% Ag/Ga₂O₃ (IMP) sample was not due to

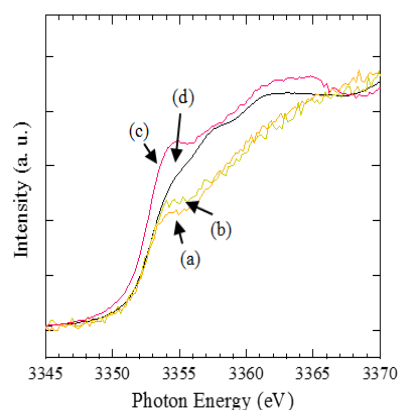


Figure 2. Ag L_3 -edge XANES spectra of the 0.1 wt% Ag/Ga₂O₃ (IMP) sample (a), the 1.0 wt% Ag/Ga₂O₃ (PD-H) sample (b), the 5.0 wt% Ag/Ga₂O₃ (IMP) sample (c) and Ag foil (d).

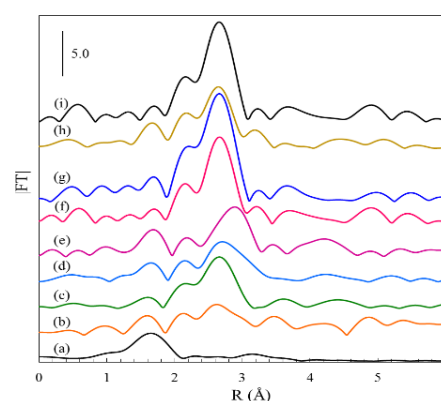


Figure 3. Radial structural functions of Ag₂O (a), the Ag/Ga₂O₃ (IMP) samples (b–f), the Ag/Ga₂O₃ (PD, PD-H) samples (g, h) and Ag foil (i). Ag loading (wt%): 0.1 (b), 0.2 (c), 0.5 (d), 1.0 (e), 5.0 (f), 1.0 (g) and 1.0 (h).

the low loading amount of Ag. Figure S1, c–f shows the Ag L_3 -edge XANES spectra of the 1.0 wt% Ag/Ga₂O₃ samples prepared by the PD method, followed by heating in air for 2 h at various temperatures, referred to as Ag/Ga₂O₃ (PD-H). A small shoulder around 3353 eV would indicate some oxidized moiety in the samples. With increasing the heating temperature, the XANES feature became broad gradually and at more than 573 K, the spectra were similar to that of the 0.1 wt% Ag/Ga₂O₃ (IMP) sample. Considering the TEM results in our previous study [8], the spectral change is assignable to the decrease of the Ag particle size by heating at more than 573 K. The decrease of the particle size suggests the strong interaction between the Ag particle and the Ga₂O₃ surface.

In Figure 2, the characteristic XANES feature just above the edge would represent the interaction between the Ag species and the Ga₂O₃ surface. The Ag/Ga₂O₃ samples showed lower absorption around 3350–3365 eV than that of an Ag bulk. This feature was most significant for the 0.1 wt% Ag/Ga₂O₃ (IMP) sample and the 1.0 wt% Ag/Ga₂O₃ heated at 623 K (PD-H) sample. Similar features around 3350–3365 eV were reported for Au–Ag alloys and Ag clusters on Au rods by some researchers [10–12]. They concluded that the electron density in the d -orbital of the Ag atom increased by transferring electrons from Au to Ag. Therefore, in the present 0.1 wt% Ag/Ga₂O₃ (IMP) sample and the 1.0 wt% Ag/Ga₂O₃ (PD-H) sample, the Ag species would probably accept more electrons in the d -orbitals from the Ga₂O₃ surface as the result of the strong interaction.

Figure 3 shows radial structure functions (RSF) obtained by Fourier transform of k^3 -weighted Ag K-edge EXAFS (Figure S2 in supporting information) in the region of $k = 3.15$ – 11.80 Å^{−1}. The small peak around 1.7 Å was assigned to the Ag–O pair and/or side lobes, and this peak was larger for the 0.5 wt% Ag/Ga₂O₃ (IMP), the 1.0 wt% Ag/Ga₂O₃ (IMP) and the 1.0 wt% Ag/Ga₂O₃ (PD-H) samples. The peak around 2.5–3 Å observed for all the Ag/Ga₂O₃ samples should correspond to the Ag–Ag pair. As for the Ag/Ga₂O₃ (IMP) samples, this peak grew with the loading amount of Ag, although it became broader and shifted to longer R region for the 0.5 and 1.0 wt% Ag/Ga₂O₃ (IMP) samples.

We also performed curve-fitting analysis on the back Fourier-transformed EXAFS from the first and the second coordination shells ($R = 1.35$ – 3.35 Å) as summarized in Table S1 in supporting information. The average Ag–Ag distance was estimated to be ca. 2.89 Å for the 0.1, 0.2 and 5.0 wt% Ag/Ga₂O₃ (IMP) samples, which was in good agreement with that of the Ag foil. Note that the photocatalytically active Ag clusters formed predominately in the 0.1 wt% Ag/Ga₂O₃ (IMP) sample were metallic. The average coordination number for the Ag–Ag shell (CN_{Ag}) for 5.0 wt% Ag/Ga₂O₃ (IMP) was close to that of Ag foil, suggesting the large Ag metal particles, while the CN_{Ag} values for the 0.1 and 0.2 wt% Ag/Ga₂O₃ (IMP) samples were 4.3 and 6.5, respectively, which were significantly smaller than that of

the Ag foil. The geometrical calculation for the 0.1 wt% Ag/Ga₂O₃ (IMP) sample demonstrated that the Ag species with the CN_{Ag} values of 4.3 would be smaller than 1 nm, such as metallic cluster, which was quite consistent with the HAADF-STEM result of this sample [8].

On the other hand, the 0.5 and 1.0 wt% Ag/Ga₂O₃ (IMP) samples had two types of short (2.89 Å) and long (3.05 Å) Ag–Ag pairs. The latter was longer than that of Ag metal and similar to the Ag–Ag distance (3.03 Å) in AgGaO₂ [13]. The Ag–O pair with 2.10–2.12 Å in length which was longer than those of Ag₂O and AgO and similar to the Ag–O distance (2.10 Å) in AgGaO₂ [13]. These suggest that a part of Ag atoms at the interface between the Ag metal particle and the Ga₂O₃ surface would be in an AgGaO₂-like structure as a result of well interaction with the Ga₂O₃ surface and other part would form Ag metal particles. In the cases of the 1.0 wt% Ag/Ga₂O₃ (PD) and the 1.0 wt% Ag/Ga₂O₃ (PD-H) samples, the average Ag–Ag distance was estimated to be 2.89 Å for both samples and CN_{Ag} for the former and the latter samples to 11.9 and 7.3, demonstrating that the large Ag metal particles changed to small ones by heating. It is also noteworthy that the Ag–O pair was found only for the 1.0 wt% Ag/Ga₂O₃ (PD-H) sample and the 0.5 and 1.0 wt% Ag/Ga₂O₃ (IMP) samples. Since another Ag–Ag pair of long distance was not recognized for the 1.0 wt% Ag/Ga₂O₃ (PD-H) sample, this Ag–O bond might be formed by the interaction of small Ag metal particles with Ga₂O₃ support.

4. Conclusion

We investigated the structural and chemical states of the Ag species as well as its interaction with the Ga₂O₃ surface by measuring Ag L₃ and K-edge XAFS of the Ag/Ga₂O₃ samples. There were some kinds of Ag species such as around 1 nm sized Ag metal cluster in the Ag low loading samples and metallic Ag particles in the Ag high loading samples. The AgGaO₂-like interface structure would be formed between metallic Ag particles and the Ga₂O₃ surface, observed in the 0.5 and 1.0 wt% Ag/Ga₂O₃ (IMP) samples. In the 0.1 wt% Ag/Ga₂O₃ sample that was photocatalytically active sample, the Ag metal clusters with the size of around 1 nm were formed predominantly, and they probably accepted more electrons in the *d*-orbitals by the interaction with the Ga₂O₃ surface. These differences in structural and chemical states of the Ag species would affect the photocatalytic activity of CO₂ reduction with water.

Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research on Innovative Areas “All Nippon Artificial Photosynthesis Project for Living Earth (AnApple)” (No. 25107515 and 15H00871) from the Japan Society for the Promotion of Science (JSPS) and the Program for Element Strategy Initiative for Catalysts & Batteries (ESICB) commissioned by the MEXT of Japan.

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